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METAL-AIR BATTERIES SYMPOSIUM

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FOREWORD

This publication includes the papers summarizing the material presented by speakers at the Metal-Air Batteries Symposium which was sponsored by the Electrochemical Working Group of the Interagency Advanced Power Group (IAPG) on 11 September 1968 at the NASA-Goddard Space Flight Center, Greenbelt, Maryland.

The Interagency Advanced Power Group wishes to express its appreciation to the authors of the various papers for their valuable contributions to the technical information exchange mission of the IAPG.

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SECONDARY CADMIUM-AIR BATTERIES

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In order to attain a maximum energy density from the cadmium-air system, sponge cadmium electrodes were developed in this program. The air-cathodes were supplied by two manufacturers who are presently fabricating state of the art electrodes. The separators were supplied by four manufacturers. No auxiliary charging electrodes were employed since the air-cathodes are bifunctional; i.e., they are charging and discharging electrodes.

The major failure modes of the cadmium-air system are: loss of capacity by the cadmium anode (fade-out), shorting by cadmium penetration, poisoning of the air-cathode and water loss.

Fade-Out Problem

When an alkaline cadmium electrode is continuously cycled on a deep discharge regime it loses capacity by a phenomenon referred to as fade-out. This phenomenon is often observed in nickel-cadmium and silver-cadmium batteries when the cells become cadmium limiting on discharge. The capacity loss is attributed to a loss in real surface area by the growth of cadmium crystals and by the subsequent blockage of the electrode pores[1,2,3].

The problem of fade-out was to a large extent overcome by the introduction of alpha ferric oxide into the active cadmium powder and by removal of CO_2 from the unit cell. As shown in figure 1 a control cadmium-air cell with a sponge negative containing no extender and exposed to CO_2 (black circles) lost 37 percent of its initial capacity in 12 cycles. A test cell (open squares) with a negative containing 5% ferric oxide and where CO_2 was removed from the unit cell was delivering 80% of theoretical capacity without any loss in capacity for 35 cycles. The combination of 5% ferric oxide extender and CO_2 exposure (black squares) resulted in the lost 30% capacity in 35 cycles, while the combination of no extender and no CO_2 exposure (open circles) resulted in a loss of 25% in capacity in 20 cycles. From these data it is seen that fade-out can be prevented by the addition of alpha ferric oxide extender to the active cadmium powder and by the removal of CO_2 from the unit cell.

The carbonate effect is again shown in figure 2. The figure shows the capacity of the sponge cadmium anode (containing 10% Fe_2O_3) as

percent of theoretical capacity versus cycle number. The prime variable was cycling in a carbonate free electrolyte (open circles) versus a carbonate saturated electrolyte (solid circles). From the figure it is seen that carbonate exposure decreased the capacity of the anode by 30 percent in 35 deep cycles, while the anode in a carbonate free electrolyte lost only 3 percent of its initial capacity in the same number of cycles.

Since carbonate increases the solubility of cadmium in 7 normal KOH by about one order of magnitude [4] it appears that carbonate accelerates the recrystallization process of the cadmium electrode [5], which at low current densities of charge and discharge results in a loss of real surface area and a subsequent blockage of the electrode pores [1,2].

Cycling data of CO_2 scrubbed unit cadmium-air cells show that anodes containing 5 to 10 percent ferric oxide extender deliver 68 to 70 percent of theoretical capacity after 100 cycles at 100 percent depth of discharge (initial efficiency was 75%). These anode efficiencies result in energy densities of 40 to 45 watt-hours per pound for unit cadmium-air cells of 10 ampere-hour capacity.

Cadmium Penetration

In table I are shown the effects of overcharge, carbonate and separator system on shorting by cadmium penetration. Group A separator wraps were employed in a carbonate saturated cadmium-air cell containing a sponge anode. Group B separator wraps were with a carbonate saturated cell containing a sintered-nickel cadmium anode. Group C separator wraps were with a CO_2 scrubbed cell containing a sponge anode. After shorting the cells were rebuilt with new separator combinations, as shown in the table.

From the data it can be seen that cadmium penetration can be minimized or prevented by: (a) minimizing overcharge, (b) preventing carbonate buildup in the cell (compare group C with groups A and B) and (c) placing a layer of Pellon between the anode and main separator (compare A1 and A2). In addition, sintered-nickel cadmium anodes appear more resistant to shorting than sponge anodes (compare B with A).

Cadmium Poisoning of the Air-Cathode

Both types of air-cathodes evaluated in this program became severely polarized towards the end of discharge in cells discharged at current densities greater than 10 MA/cm^2. On subsequent recharge the cathodes were reactivated and exhibited a normal E-I discharge response versus the fully charged cadmium anodes. However, versus nearly fully discharged cadmium anodes the air-cathodes become inactive. Even when a fresh uncycled air-cathode was discharged against a nearly fully discharged cadmium anode the cathode became inactive.

Chemical analysis indicates the presence of cadmium in the air-cathode after cycling-the concentration of cadmium in the cathode was 0.1 mg/cm^2. It is believed that during the end of discharge the cadmium anode increases the concentration of soluble cadmate ion ($Cd(OH)_3^-$) in the electrolyte to a quantity sufficient to poison the air-cathode. This is presently being explored by chemical analysis of the electrodes and electrolyte. This poisoning occurs when the electrolyte is free of carbonate ions or other impurities. Figure 3 shows that when the electrolyte is saturated with carbonate ions inactivation of the air-cathode will not occur. For comparison, the figure includes the polarization of the air-cathode and cadmium anodes in pure 7 normal KOH (open circles) and 7 normal KOH saturated with carbonate (solid circles).

It is reported that cadmium forms a soluble cadmium carbonate species $Cd(CO_3)_3^{-4}$, which is about ten times more soluble than the cadmate ion in 7 normal KOH[4,6]. Apparently the cadmium carbonate species is beneficial to the air-cathode in that it prevents poisoning by the cadmate ion. However, as was shown in the Figure 2 carbonate severely decreases the capacity of the cadmium anode (after 20 cycles) and therefore is not desirable as an additive to the electrolyte. Consequently, a search was made for electrolyte additives which would: (a) prevent poisoning of the air-cathode by cadmium and (b) would be innocuous to the cadmium anode.

One such additive has been found. As shown in Figure 4, when the electrolyte is saturated with zincate ion the air-cathode will not inactivate at the end of discharge and the electrical efficiency of the anode is not impairedafter 10 deep discharge cycles. Since overcharge did not show a zinc deposition step it is apparently safe to saturate the electrolyte with zincate in a rechargeable cadmium-air cell. I might add that aluminate has also been found to prevent cathode poisoning. At present cadmium-air cells with zincate electrolyte are being life cycled and other additives are being screened in an effort to understand and better control the poisoning effects of the air-cathode.

Water Loss and Unit Cadmium-Air Cell Design

The 10 ampere-hour unit cadmium-air cells lost about 0.5cc of water per cycle at the C/5 rate of charge and discharge. As shown in Figure 5, a prototype 10 ampere-hour unit cell design includes a sump at the base of the cell which contains 5cc of reserve electrolyte (as water). The excess water would prevent drying of the cel' for about 10 cycles (the unit cells cycled in this program had a sump with 100cc of excess electrolyte). The battery could be watered every 10 cycles through a filling hole in the cover, after unscrewing the sealing plug. The required amount of water could be indicated by constructing the cell with a transparent or translucent plastic frame through which the electrolyte level can be seen and adjusted.

Electrolyte adsorbent polyamide Pellon is placed in both the anolyte and catholyte compartments to transport electrolyte from the sump to the electrodes. The main separator consists of two layers of a non-oxidizable and non-degradable membrane, such as Astroset 3420-09 or RAI, P-300. The anode is 100 mils thick, with an apparent porosity of 62%, and contains 5% ferric oxide extender and 5% carbonyl nickel conductor. The air-cathodes are bifunctional with a platinum loading not exceeding 6 mg/cm^2. The electrolyte is 30% KOH saturated with zincate. To prevent carbonate buildup in the cell replaceable ascarite air spacers can be attached to the air faces of the air-cathodes or barium hydroxide can be added to the base of the sump.

An actual 24 volt, 25 ampere-hour cadmium-air battery is being constructed by General Electric for the US Army Electronics Command. The battery is being built according to the design parameters that were derived from this program. It is estimated that the unit cells will have an energy density of 45 watt-hours per pound at the C/5 rate and the battery plus case hardware will have an energy density of 35 watt-hours per pound. At present, a test cell has exceeded 300 deep discharge cycles[7]. Therefore, the goal of 500 cycles for the battery can be anticipated.

Conclusions

1. Loss of capacity by the cadmium anode can be prevented by use of ferric oxide extender and removal of CO_2 from the cell.

2. Cadmium penetration can be prevented by removal of CO_2 from the cell, minimizing overcharge and placing an inert electrolyte absorbent inter-separator between the cadmium anode and main separator.

3. Poisoning of the air-cathode can be prevented by using KOH electrolyte saturated with zincate.

4. Water loss can be compensated by providing the unit cell with an electrolyte sump.

5. Unit cadmium-air cells have been built with a cycle life greater than 300 cycles and an energy density in the range of 40 to 45 watt-hours per pound.

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Table I - The Effect of Overcharge, Carbonate and Separator System on Cadmium Penetration.

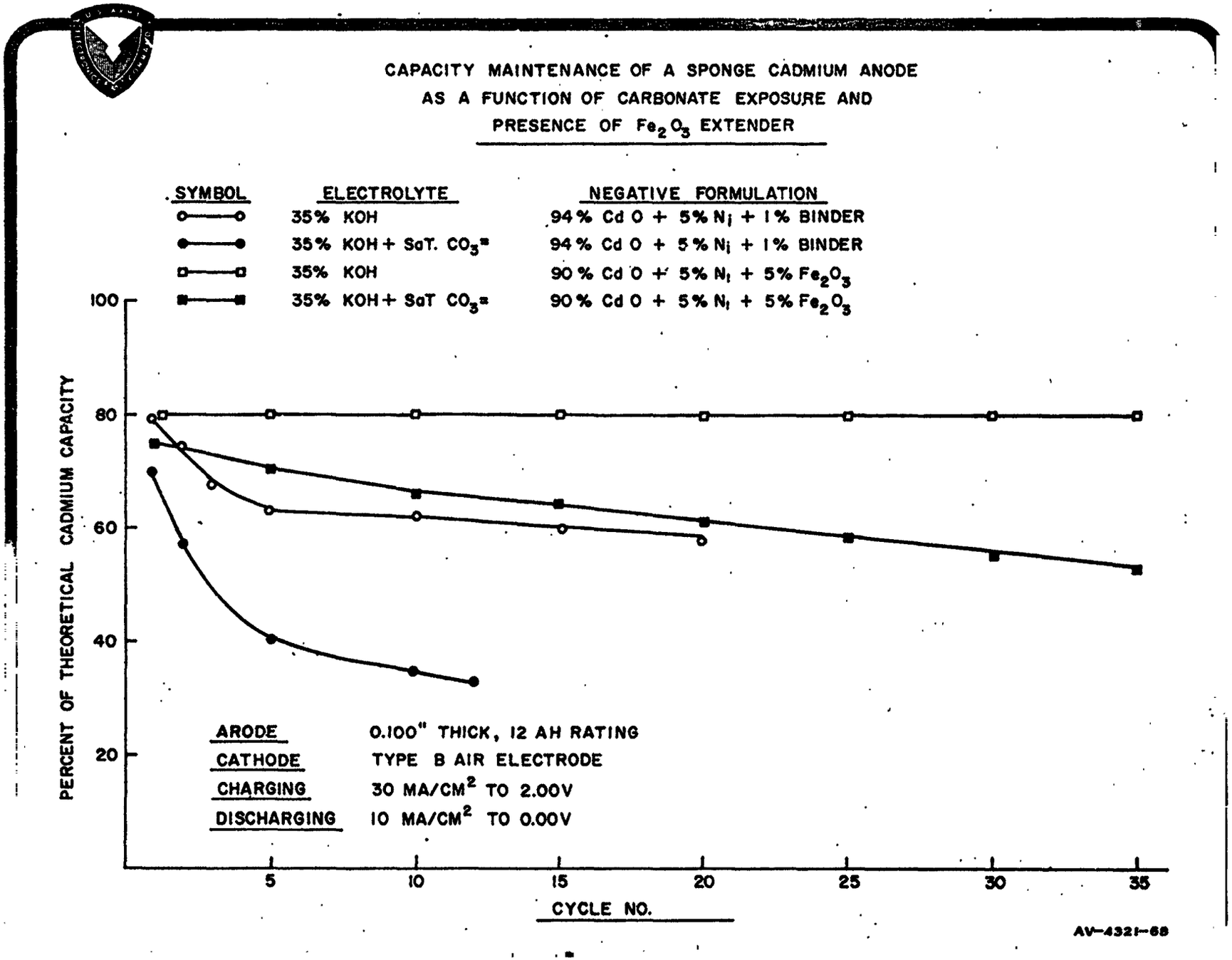
	Separator System	Cycles to Short	Total AH of Overcharge
A	Sponge Cadmium - Air Cell ($CO_3^=$ Saturated)		
A1	(+) 1 X .001" Cellophane/1 X .006" Pellon (-)	58	48
A2	(+) 1 X .006" Pellon/2 X .001" Cellophane (-)	9	5
A3	(+) 1 X .006" Pellon/2 X .002" Astroset /1 X .006" Pellon (-)	75	76
B	Sintered Nickel Cadmium-Air Cell ($CO_3^=$ Saturated)		
B1	(+) 1 X .006" Pellon (-)	98	56
C	Sponge Cadmium-Air Cell (No $CO_3^=$ In Electrolyte)		
C1	(+) 1 X .006" Pellon/2 X .002" Astroset /1 X .006" Pellon (-)	120 + (still cycling)	180 +
C2	(+) 1 X .006" Pellon/1 X .0015" RAI P300 /1 X .006" Pellon (-)	20 + (still cycling)	20 +

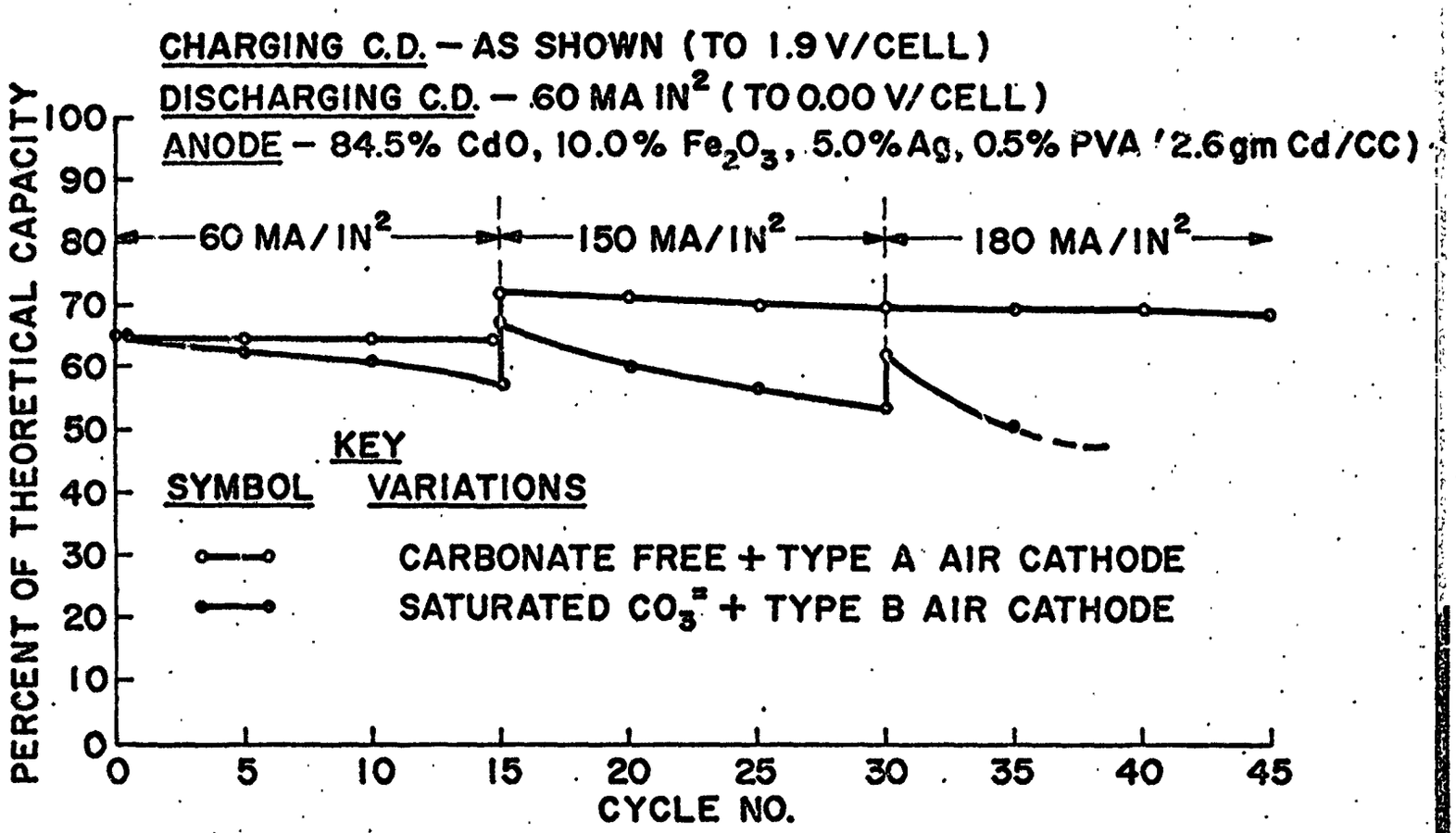
Figure 1

Capacity Maintenance As A

Function Of Cadmium Mix

and CO_2 Exposure


CAPACITY MAINTENANCE OF A SPONGE CADMIUM ANODE
AS A FUNCTION OF CARBONATE EXPOSURE AND
PRESENCE OF Fe_2O_3 EXTENDER
SYMBOL
ELECTROLYTE
NEGATIVE FORMULATION
35% KOH
94% Cd O + 5% Ni + 1% BINDER
35% KOH + SaT. $CO_3^=$
94% Cd O + 5% Ni + 1% BINDER
35% KOH
90% Cd O + 5% Ni + 5% Fe_2O_3
35% KOH + SaT $CO_3^=$
90% Cd O + 5% Ni + 5% Fe_2O_3
PERCENT OF THEORETICAL CADMIUM CAPACITY
100
80
60
40
20
ARODE
0.100" THICK, 12 AH RATING
CATHODE
TYPE B AIR ELECTRODE
CHARGING
30 MA/CM^2 TO 2.00V
DISCHARGING
10 MA/CM^2 TO 0.00V
5
10
15
20
25
30
35
CYCLE NO.
AV-4321-68



CAPACITY MAINTENANCE AS A FUNCTION OF CARBONATE EXPOSURE AND CHARGING CURRENT DENSITY

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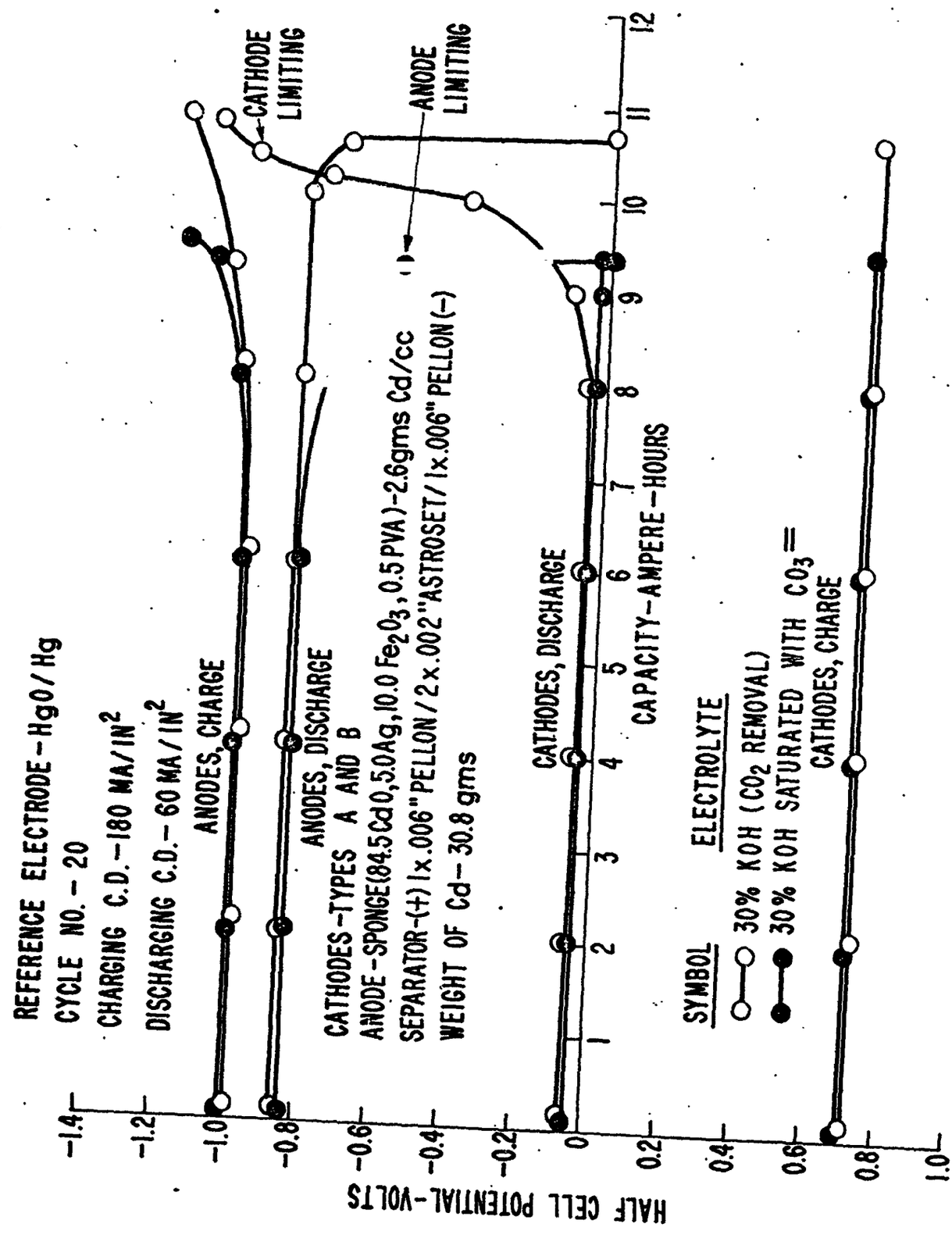
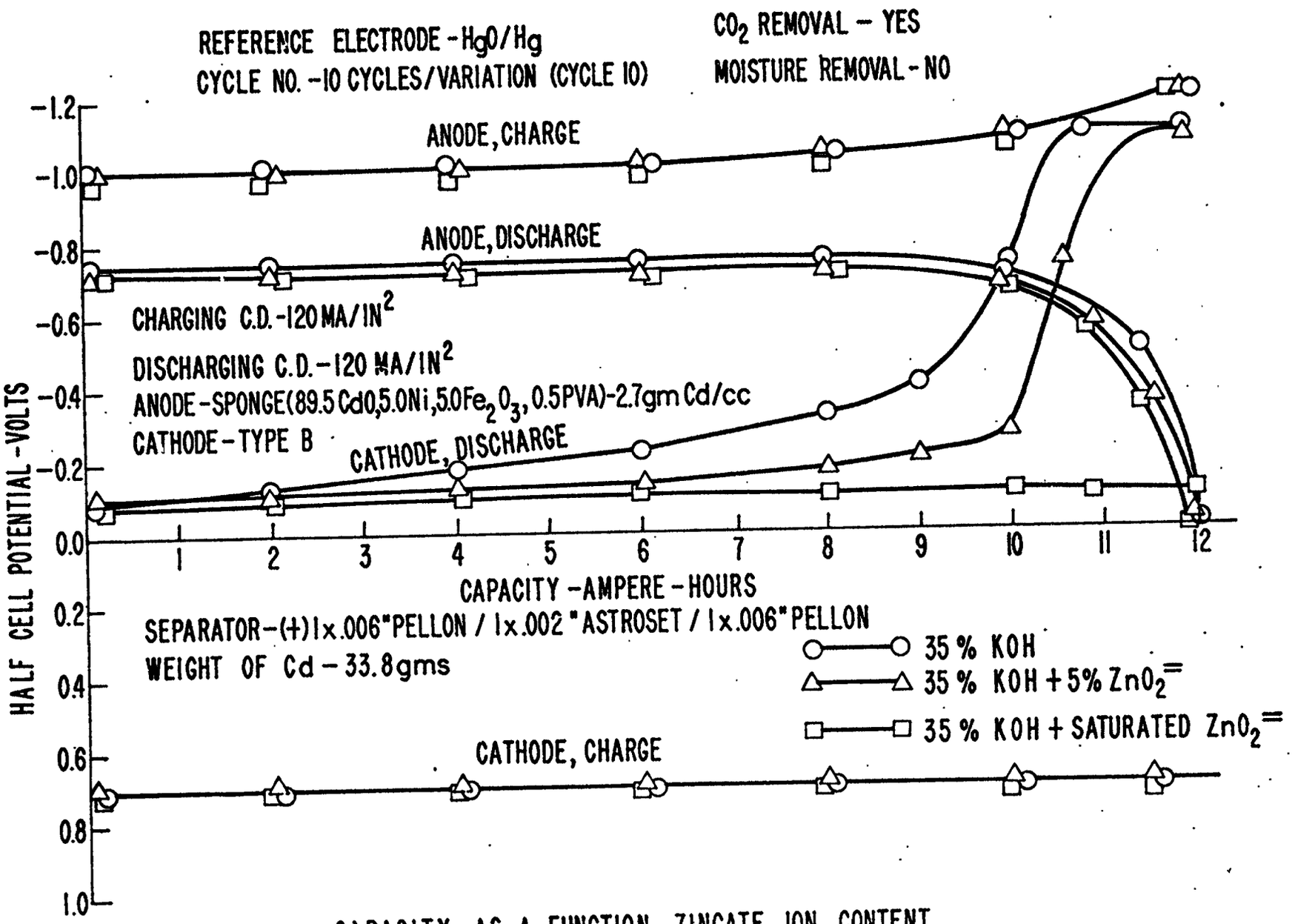


CAPACITY AS AFFECTED BY CARBONATE IN THE ELECTROLYTE



CAPACITY AS A FUNCTION ZINCATE ION CONTENT

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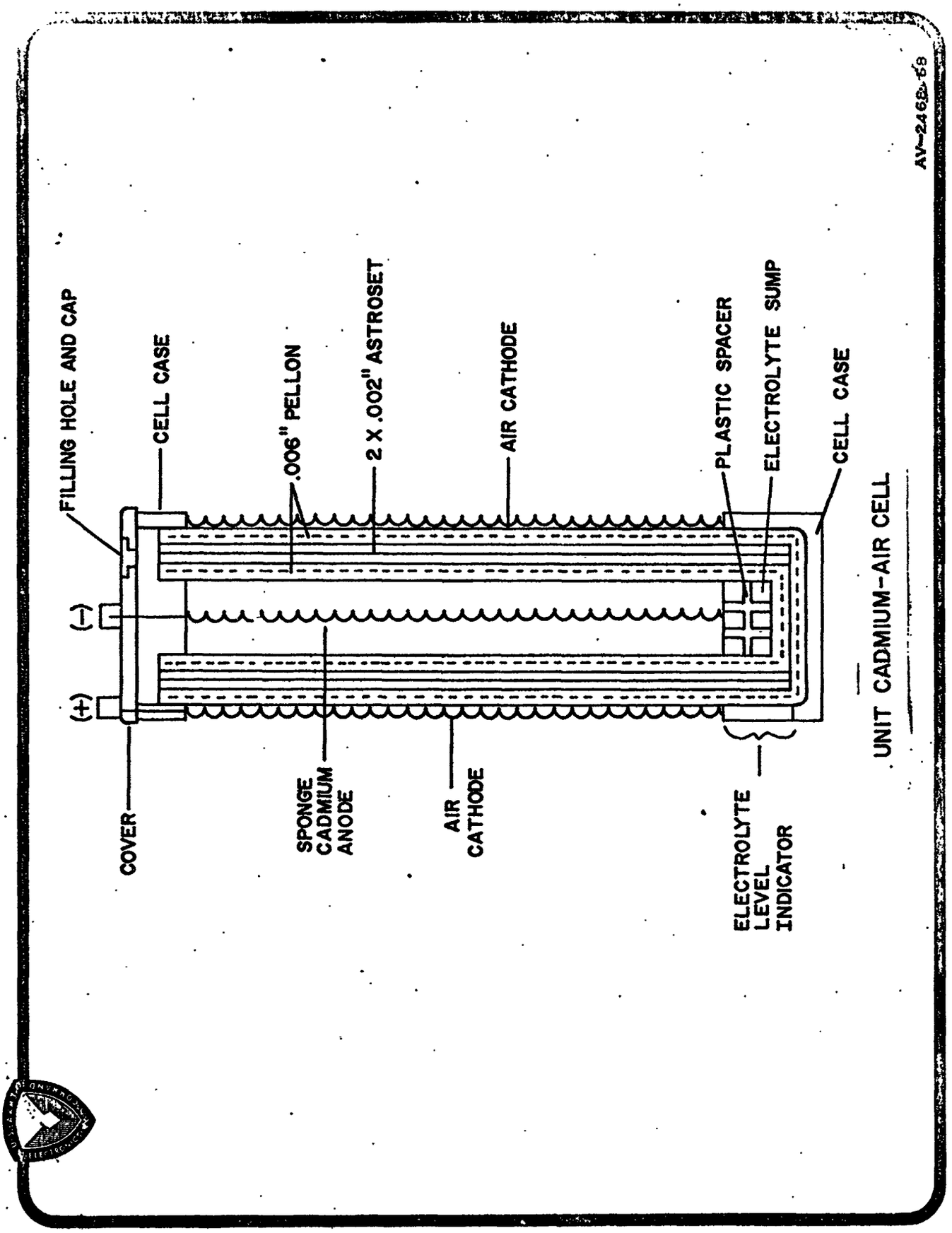

UNIT CADMIUM-AIR CELL

SECONDARY IRON-AIR BATTERIES

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In order to attain a maximum energy density from the iron air system, non-supported active iron-electrodes must be developed. The theoretical energy density of the iron anode for the iron-to-ferrous state is 556 watt-hours per pound; for the iron-to-ferric state the total theoretical energy density is 837 watt-hours per pound. To utilize the three electron change the system will discharge on two voltage plateaus; namely, 0.8-0.9 volts for the Fe/Fe^{++} reaction and 0.7-0.6 volts for the Fe^{++}/Fe^{+++} reaction. The two voltage plateaus are disadvantageous for most portable power applications, although the energy realized from the total reaction is very attractive.

Another major advantage of the alkaline iron system is that iron is cheap and very abundant as a raw material. This factor is of greatest importance in addition to its high theoretical energy density. The long cycle life of the alkaline iron anode (more than 20 years of service in Edison Ni/Fe batteries, for example) provides another attractive feature for this system.

An important limitation of the iron-air system, employing the conventional iron anodes, is that its shelf life is very poor. This is due to the low hydrogen overpotential of the electrode. In addition, the conventional iron electrode requires 50-60 percent overcharge to attain maximum electrochemical utilization of the active material. This results in an appreciable loss of water, which means that a conventional alkaline iron-system would require considerable maintenance.

Approaches to overcome the limitations of the alkaline iron system have been reported by many investigators, and it appears that an iron-air and/or other alkaline iron systems can be developed to meet the needs of present day portable power requirements.

The major failure modes reported in the literature for the iron-air system are: (a) self-discharge, (b) oxidation of the anode, (c) loss of active material utilization on deep discharge and reverse discharge and (d) water loss.

The first topic is Self Discharge - The self discharge of the iron electrode is mainly caused by the couple action between the low hydrogen overpotential impurities on the electrode and the active iron powder. (1) Burshtein reports that this self-discharge can be reduced to minimal rate by partially passivating the electrode by treating it with benzene or other volatile organic liquids (2). It is also reported that the electrode can be beneficially treated by the addition of 1% water glass or sodium phosphate inhibitors to the electrolyte.

The self-discharge of the alkaline iron electrode is accelerated by the employment of nickel powder conductor material or other low hydrogen overpotential materials. Therefore, to provide the electrode with a conductive matrix which does not induce self discharge it is necessary to employ materials (in addition to the conductive Fe of the electrode itself) with hydrogen overpotentials higher than that of alkaline iron. In addition, the conductor must not form resistive oxide layers, or dissolve in the electrolyte. Mercury and copper have been beneficially employed in the conventional iron electrodes of the pocket or tubular types. Since these metals possess hydrogen overpotentials in alkaline electrolytes higher than that of iron it is possible that they provide the desired conductive matrix. Other effects such as extender or expander action are also possible.

The second topic is Oxidation of the Anode - Oxidation of the anode by air is a problem common with all metal-air systems. Methods to overcome this problem are: cladding the anode with semipermeable membranes and constructing the unit cell so that air can have access to the system only through the pores of the air cathode; that is, the unit cells must be designed as sealed structures.

The third topic is Loss of Active Material Utilization - It is known that pure alkaline iron systems, where the iron electrode is limiting on discharge, lose capacity by irreversible electrochemical reactions. It is reported in the literature that the active material utilization of iron powder is stabilized and increased by the use of graphite (3), molybdenum (4), tungsten (4), and sulfur additives. These additives may be beneficial by reducing the self-discharge reaction of the iron anode and/or providing expander and/or extender action.

Water Loss - The problem of water loss is common for all metal-air systems. For iron-air it is serious because of the self-discharge reaction and the need for extensive overcharge. Methods to minimize this problem are: (a) reducing the self-discharge reaction of alkaline iron (as previously discussed), (b) improving the active material utilization of the iron anode so that it is highly reversible and (c) providing the unit iron-air cell with a reserve of excess electrolyte in a reservoir.

Performance Characteristics of the Iron-Air System - General Telephone and Electronics has been pioneering the development of a practical iron-air system during the past several years. They report that they have developed iron-air cells of 5 to 20 ampere-hour capacities with a cycle life greater than 200 cycles at energy densities of 60-70 watt hour/pound. The regime was at 65 percent depth of discharge at the C/2 rate (5). As with the ECOM cadmium-air system the air cathode of the GT&E system was a bifunctional platinum electrode.

Up to the present time, R&D efforts at ECOM with the iron-air system have been very limited. Exploratory work has been done with iron electrodes supplied by GT&E and air cathodes by Leesona Moos. Data have been erratic and nonconclusive. Work will be carried out in the near future utilizing the knowledge of the present state-of-the-art of the electrodes as well as novel approaches derived from internal work.

Conclusion - If the self-discharge, capacity maintenance, oxidation and water loss problems of the iron-air couple are resolved, this system should become very attractive as a low cost, high energy density power source for communication and transportation applications.

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ZINC-AIR BATTERIES

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Good results have been obtained to date with zinc as the anode in primary zinc-air or zinc oxygen batteries. Zinc electrodes in thicknesses up to 1/4", are operating at 60% or better of theoretical efficiency with regularity. These batteries yield energy densities in the order of 80-150 WH/lb.

Either noble or non-noble metal catalyzed air or oxygen electrodes may be used for primary batteries. In general, Pt is used as the catalyst in "refuelable" batteries, while carbon, nickel, silver, and silver-amalgam are used for one-shot types. The general mode of operation for the one-shot battery is to add water to activate. However, it is more desirable to store the battery wet and activate by admitting air. For an air activated battery the storageability of the zinc electrode as well as the wetting characteristics of the air electrodes become important considerations.

Zinc electrodes must be heavily amalgamated to prevent self discharge and the evolution of hydrogen. The recrystallization properties of zinc and zinc oxide must be taken into account since crystal growth during long term stand, particularly at elevated temperatures, can partially passivate the zinc electrode. Therefore zinc electrode characteristics must be determined and controlled before activated storage zinc-air batteries are completely feasible.

In order to use the zinc-air system as a secondary battery one basic characteristic of zinc must be overcome. This is the fact that zinc, unlike other secondary battery electrodes such as Ni, Ag, Fe, and Cd, has a relatively high solubility in alkaline electrolyte. With oxidized zinc species being soluble. In addition, zinc tends to supersaturate the electrolyte during anodization to a value approximately 2 times the equilibrium value.

The high zinc solubility leads directly to such failure causing mechanisms, as zinc electrode shape change, dendrite growth and separator penetration, and the precipitation of zinc oxides in the air electrode.

"Shape change" is the loss of geometric surface area due to sluffing off and redistribution of zinc with cycling. This leads to the densification of the zinc metal formed on charge at the surface of the electrode, thus preventing full utilization of the remaining zinc oxide. Shape change

therefore results in a gradual loss of capacity and voltage with cycling until such time as the limiting current density is exceeded and then capacity rapidly falls below minimum levels.

Shape change tends to be more severe in secondary zinc-air cells than in Ag-Zn. This occurs because in the air system the zinc electrode is limiting on both charge and discharge. This causes the zinc to be fully worked each cycle rather than only 1/3 to 1/2 utilized as is the case in Ag-Zn. Therefore the shape maintenance effect of reserve zinc oxide is not available in Zn-air batteries.

Steps that can be taken to minimize shape change include the addition of binders. Particularly good results have been obtained with Teflon, as developed by the Yardney Electric Company (see reports on Contract DAAB07-67-C-0185). Minimization of the amount of amalgamation has also reduced shape change, although some Hg is required to prevent self discharge. Hg contents of the order of 0.5-1.0% appear optimum.

Another development from the Ag-Zn system that should prove useful in reducing shape change is the use of zinc electrodes having a larger geometric area than the positive electrodes. These oversized zinc electrodes appear to be effective in reducing edge effects which are points of higher potential and faster dissolution. Based on results obtained in silver-zinc cells it would appear that shape change can be minimized sufficiently to provide a life of more than 100 cycles, with 300 cycles a distinct possibility.

However, even if shape change is controlled the problem of separator penetration by zinc dendrite growth must be overcome if adequate cycle life is to be maintained. To date most of the conventional film type separators tested have not proved adequate. These include cellophane, fibrous sausage casing, poly (vinyl methyl ether/maleic anhydride) in a methyl cellulose base, and radiation grafted polyethylene. These materials have all been subject to oxidative attack by nascent oxygen or have high resistance which accentuates shape change. However, inorganic separator materials as developed by Douglas and more recently by other companies have shown promise as non-oxidative materials that are capable of preventing zinc penetration. Over 50 deep cycles have been obtained to date with these materials without failure.

Zinc dendrite growth may also be minimized by limiting overpotential on charge. Studies by McBreen have indicated that 70 mV overpotential above rest potential is sufficient to cause dendrite growth. Fortunately, zinc is a highly active electrode and does not reach this level except at the end of charge.

One failure mode that is unique to the Zn-air system is zinc oxide precipitation in and on the air electrode. The figure shows the solubility of zinc as a function of KOH concentration. Precipitation can occur at the end of charge when the electrolyte in the air electrode compartment is dilute from the generation of water. However, it is more likely to occur at the end of discharge when the electrolyte is very concentrated and large amounts of soluble zinc are available. The precipitation of zinc oxide in the air electrode is more likely to occur if a random cycling regime with long stand periods is followed rather than on rapid automatic cycling since rapid cycling tends to minimize the swings in electrolyte concentration. This leads to a critical current density for zinc-air batteries above which zinc oxide precipitation occurs, changing the wetting characteristics of the air electrode. This current density value may be considerably lower than the polarization behavior would indicate. However, this critical value is dependent on such factors as separator type, cycling conditions, and temperature, etc.

The air electrode for secondary zinc-air batteries appears to require the use of noble metal catalysts such as Pt, if auxiliary charging electrodes are to be avoided. This is desirable since it is calculated that, for a fixed volume, energy density will be reduced by approximately 1/3 if an extra charging grid is used.

To summarize, Zn-air secondary batteries appear capable of energy densities of 75-100 watt-hours/lb and can operate for 100 or more cycles using separators of the inorganic type. Much more work is required to optimize the air-zinc system and to determine its limiting use conditions.

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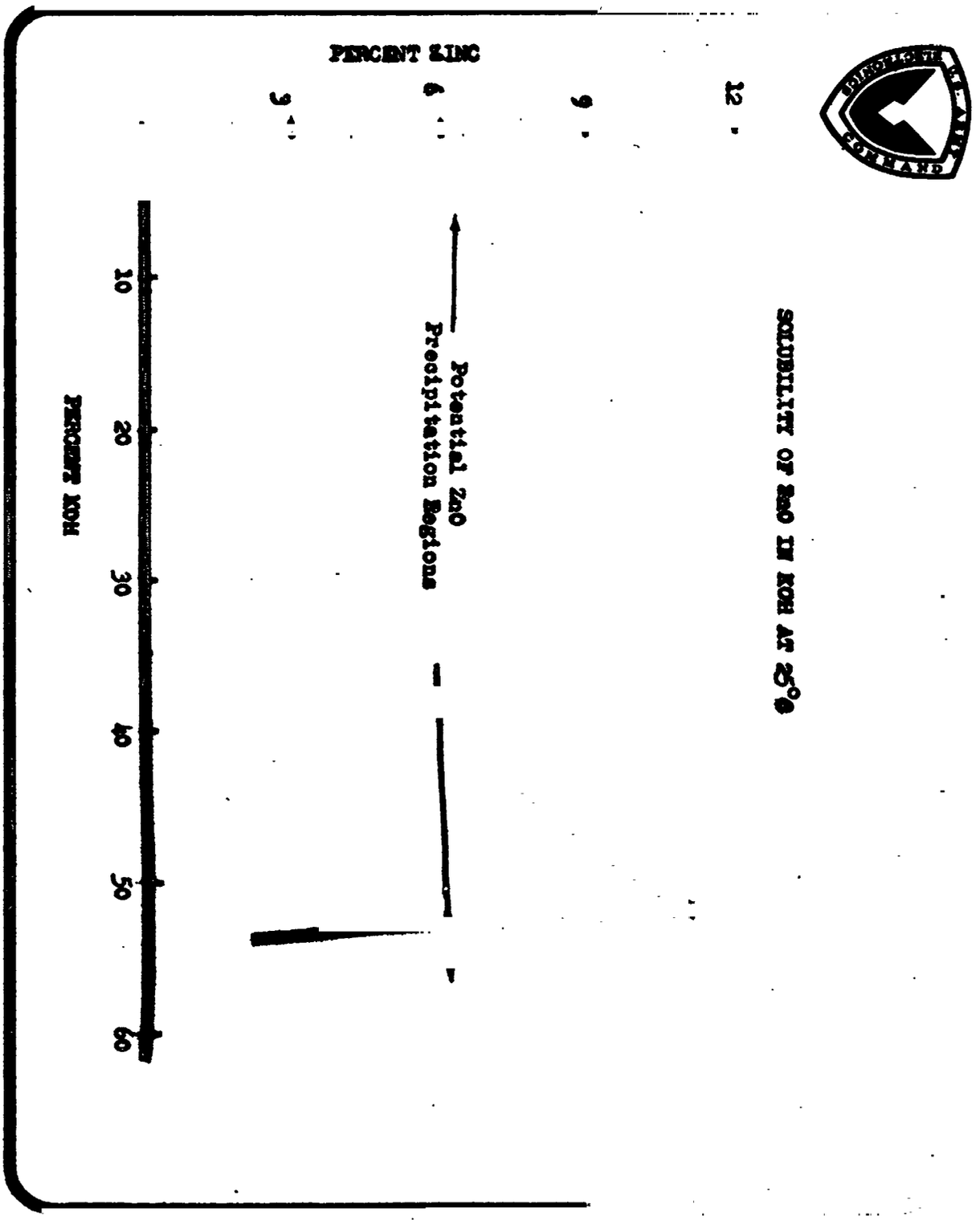

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MAGNESIUM-AIR BATTERIES

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Among the anodic materials considered for use in metal-air batteries, magnesium ranks second only to zinc in characteristics deemed suitable for use in portable power supplies. From a theoretical point of view, magnesium would appear to rate higher than zinc, having both a higher thermodynamic potential and a higher calculated coulombic capacity per unit weight (Mg-1000 A.H./lb vs Zn-372 A.H./lb). However, practical considerations in past studies have shown that magnesium does not produce its theoretical potential in aqueous solutions and because of undesirable, and to some extent, uncontrollable side reactions does not provide its theoretical coulombic capacity either. For optimum use as a battery anode, magnesium should be used in solutions having a pH range from 6 to 9. Below pH 6, hydrogen formation becomes quite rapid and chemical corrosion consumes the major portion of the anode to the detriment of the electrochemical coulombic efficiency. Above a pH of 9, magnesium metal passivates through oxide or hydroxide film formation which acts as an insulating layer and electrochemical activity is inhibited severely.

There is, of course, no difficulty in obtaining solutions falling within the proper range of pH. General Electric Company pursued the use of sodium chloride solutions and achieved some measure of success at temperatures above freezing. The optimized solution of sodium chloride freezes at approximately 25°F. Prototype batteries were built and operated. Current levels were not as high as hoped for, and voltage transients produced some difficulties in achieving good voltage regulation in the battery. Excess water requirements also caused greater battery volume and weight than was originally estimated. These difficulties along with some component designs will require further investigation which could not be made under the time stresses of the original program. This work did point out the feasibility of a high rate, high energy density magnesium-air battery producing 50 watt-hours per lb.

In research studies for USAECOM, Yardney Electric Company, after a limited investigation of several salts, settled on use of a 3:2 eutectic of 4 N sodium-lithium perchlorate solution which was found advantageous in operation to -15°F. At -15°F, approximately 33% of room temperature capacity is obtained. Room temperature capacity approaches only 65% coulombic efficiency of the magnesium anode because of the corrosion resulting from chemical interaction of magnesium and water. At 125°F this undesirable

side reaction increases and only 40% of the nominal capacity is obtained. Figure 1 shows the effect of temperature on the cell voltage in the magnesium-air system using mixed perchlorate electrolyte.

Current densities with the magnesium-air system are not as high as with the zinc system. Because of the resistivities of the electrolyte and the air cathode, and the use of sheet magnesium rather than the highly porous structure anode (as used in the zinc system) about 25-30 ma/cm^2 is optimum current density for efficient use in the magnesium-air system. Cell voltages of 1.24-1.28 volts are obtained at current densities of 12 ma/cm^2 (80 ma/in^2). Figure 2 shows the effect of current density on the cell voltage in the magnesium-air system using perchlorate electrolytes.

In battery structures, the need for precise and proper designs is much more stringent in magnesium-air batteries than in zinc systems. Volume considerations especially must be viewed judiciously. The interelectrode spacing requirement, for example, was found to be 3 times the thickness of the magnesium sheet, i.e., the required interelectrode distance was 170 mils for a 55-60 mil thick magnesium anode. The large volume requirement is the result of the need for a much greater quantity of water in the magnesium system than for the zinc system. There is at least a threefold reason for the excess water requirement; to accommodate the voluminous reaction product ($Mg(OH)_2$ evolving from both electrochemical activity and from the uncontrollable chemical interaction of magnesium and water, to allow for the inherent water vapor evaporation through the cathode walls and, of course, to provide an ionic medium for cell reaction. It is mainly this excess of water that reduces the energy density of the magnesium-air system. Electrolyte in the magnesium system amounts to 80-85% of the weight of the active materials whereas in the zinc system only 30-35% is required for the electrolyte.

Despite the above difficulties these studies show that magnesium-air batteries can be produced having energy densities on the order of 50-55 watt-hours per lb.

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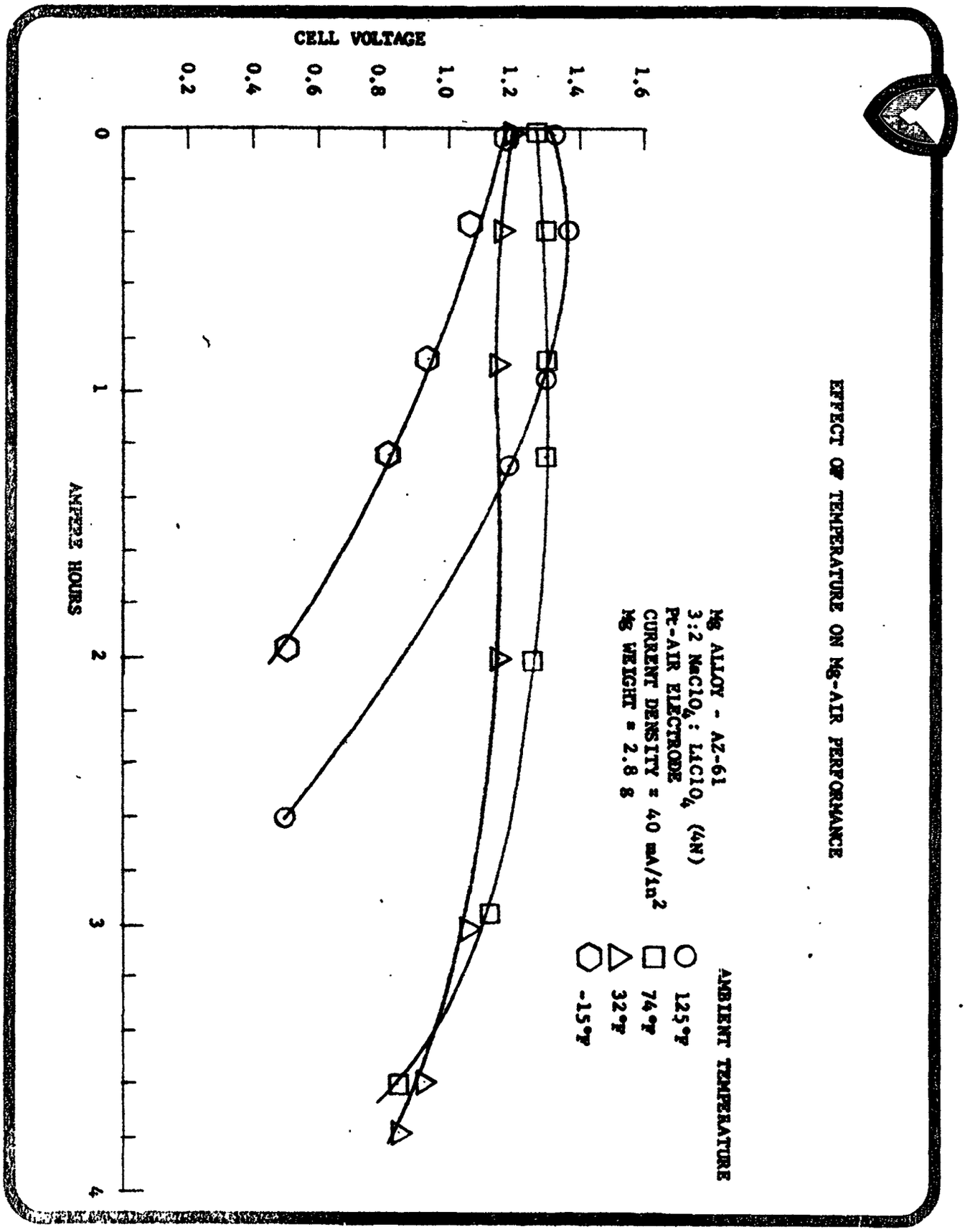

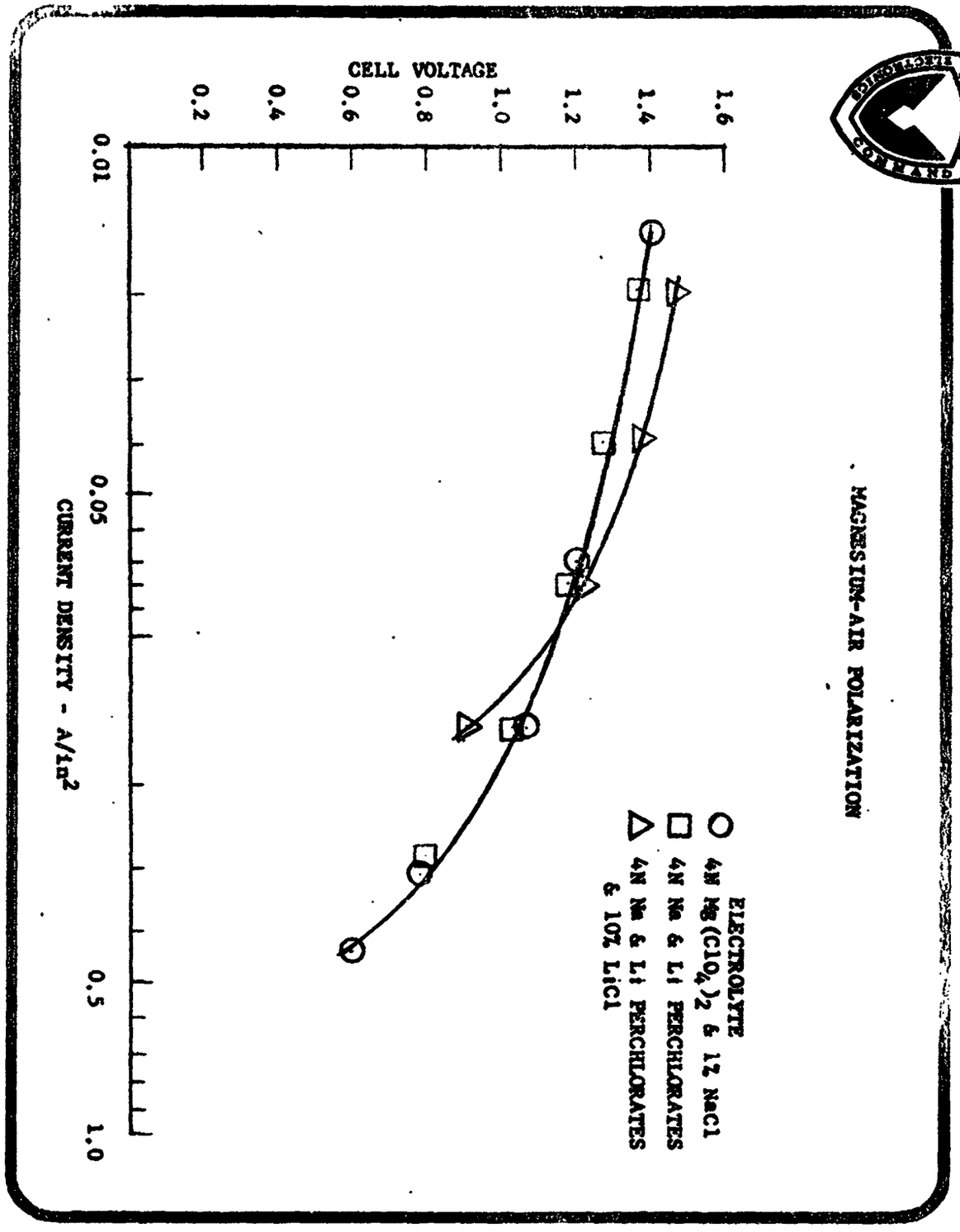

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LITHIUM ANODE
by
Dr. J. Toni

The application of lithium as anode in a metal-air battery can only be conceived using an aprotic media. If one refers to organic aprotic solvents as the aprotic electrolyte there is not any doubt that Li is the most popular and promising anode available. It is also well known the considerable government effort in the development of high energy organic electrolyte batteries which practically in any case include Li as the postulated anode. In fact, Li has a very low equivalent weight of 6.9 and it should produce one of the lightest weight practical anodes. In addition, it has a high equivalent potential of around -3 volts dependent of the electrolyte used. The electrode has been found to be reversible in several electrolytes. For example, potentiometric studies in LiCl-Dimethylformamide (DMF) showed that the potential obeys the Nernst equation over a wide concentration range, between $10^{-4} < C < 1F$. The relationship between current and potential for Li electrodes has been measured under steady-state conditions in a number of different electrolytes. In general, it has been found that the polarization of this electrode is small and apparently it is more related with the solvent than with the solute. The exchange current density for Li was measured in electrolytes containing, PC (propylene carbonate), BL (butyrolactone), DMF (dimethylformamide), DMSO (dimethyl sulfoxide), and PC-NM (nitro methane) mixtures. The value was in the order of 1 ma/cm^2 which is a quite high exchange current value and supports the reversibility of this anode. A number of electrode configurations are being considered in the development of test cells. The methods of electrode preparation have included the following:

a. Pressing or rolling Li ribbon onto metal screen made of copper, silver, nickel and aluminum.

b. Pressing lithium powder with or without conducting additives onto metal screens.

c. Dipping nickel screen into molten lithium. Apparently the former method is the one which has given better results in terms of least polarization and highest efficiency.

Research in primary systems has shown that the coulombic efficiencies of lithium anodes are in general very high; they vary between 70-100%. Relative high current densities have been sustained on Li electrodes, for example, 30 ma/cm^2 is quite normal and relatively easy to achieve; values up to 100 ma/cm were also reported. Considerable work has been done on the possibilities of Li in secondary batteries. The reported data are promising, but at best the cycling efficiency for lithium electrodes appears to be about 85%. There is a clear tendency to decrease as the number of cycles increases. The reasons for low cycling efficiency are not entirely understood, however, the processes most likely responsible may be: mechanical loss of electrodeposit Li; loss of electrical contact during anodic discharge due to a

preferential attack at the base of Li dendrites; alloy formation with the substrate material or occurrence of side reactions which would not produce electricity. It should be pointed out here that practically all the work reported about Li oxidation was done with solvents which in few of the best cases had approximately 50 ppm of water, but in general were much more contaminated with it. Concentrations of 500-1000 ppm were very frequent. These quantities appear to exert minor effect on the discharge of Li, but the reasons are not clearly understood yet because water may form lithium hydroxide which can passivate the electrode.

Related with the development and possibilities of the couple Lithium-Air the only source available under my knowledge is a contract performed by Globe-Union between March 1966 to June 1967 with USA Mobility Equipment Research and Development Center, Fort Belvoir, Va. The intention of the contract was the analysis of the couple in order to develop a high energy secondary battery. Unfortunately the contract was not continued enough to permit a complete evaluation of the system. During the contract period a major emphasis was imposed on the behavior of the air electrode in organic electrolyte and only initial data was obtained about the negative electrode. The reason of this priority was that at that time very little was known about the kinetics of O_2 reduction in aprotic solvents in opposition of a fairly large volume of data related with the Li anode. The postulated couple included also water as moisture and the system was called Lithium-moist Air Battery. The induction of water was postulated in order of the Li tolerance of water and with the intention to transform the oxygen reduction products in hydroxide and also permit the formation of LiOH which was considered insoluble and should be formed on the anode surface. This last picture would help the development of a secondary battery. The overall expected reaction was

$$2Li + 1/2O_2 + H_2O \rightleftharpoons 2LiO_4$$

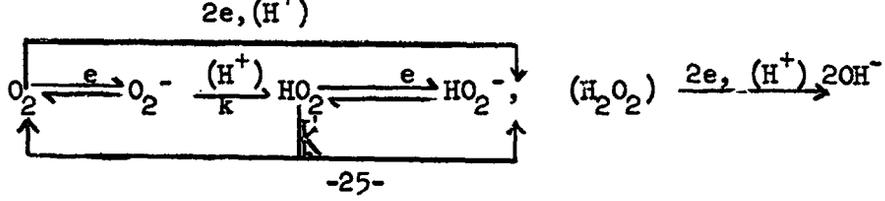
The research was carried out principally on one solvent, NDA, nitrosodimethylamine, an interesting aprotic solvent, but with very toxic properties. The experimentation was performed using two solutes: $LiClO_4$ and a tetra substituted ammonium compound; phenyl-trimethyl ammonium hexafluorophosphate ($PhMe_3\ NPF_6$). The study of oxygen reduction turned out to the postulation of a very complex mechanism which included first, a series of surface processes on the electrode (adsorption, interaction between oxygen and platinum, reduction of the film formed) and second two partially mass transport dependent steps with chemical kinetics complication (E.C.E.). Superoxide and peroxide were postulated as intermediates:

SURFACE PROCESS

$$O_2 \rightleftharpoons O_2 \text{ surface}$$

$$O_{2\,surf} + Pt \longrightarrow O_xPt_y$$

OXYGEN REDUCTION



The effect of increasing water concentration was studied in detail and it showed that the overall mechanism of oxygen is very much affected by water availability. Apparently a reaction similar to the one in aqueous media occurs only at H_2O concentration over 1%. At this concentration the current capabilities achieve also a maximum value.

During the last part of the contract few experiments were run in order to test the compatibility of the overall system. Initial experiments using the electrolyte $PhMe_3NPF_6$-NDA showed that the air electrodes can support current densities up to 20-30 ma/cm^2 while Li independently, in the same electrolyte, was discharged at 30 ma/cm^2. The whole system using small laboratory scale cells was discharged at low current densities (2-5 ma/cm^2) for short time. Apparently there is compatibility of anode and cathode and a 2 volt battery might be possible.

From these data some ideas can be postulated about the possible development of the battery. The minimum level of water concentration for full current capabilities of the O_2 electrode is too high for the behavior of the Li anode. This problem would require the development at lower concentration of water with the consequent decrease in current capabilities of the air electrode and the possibility of building up superoxide and peroxide compounds. Engineering design may permit a separation of catholyte and anolyte in order to allow the behavior of each electrode at different water concentration.